

THERMOPHYSICAL PROPERTY MEASUREMENT OF MOLTEN SILICON BY HIGH TEMPERATURE ELECTROSTATIC LEVITATION

o Won-Kyu Rhim, Sang K. Chung, Aaron J. Rulison¹⁾, and R. Erik Spjut²⁾

Jet Propulsion Laboratory,
California Institute of Technology,
4800 Oak Grove Drive, Pasadena, California, 91109 USA

ABSTRACT

Several thermophysical properties of molten silicon measured by the High Temperature Electrostatic Levitator (HTESL) are presented. They are density, constant pressure specific heat capacity, hemispherical total emissivity, and surface tension. Over the temperature region investigated (i.e. $1350 \text{ K} < T_m < 1825 \text{ K}$), the measured liquid density is expressed by a quadratic expression:

$$\rho(T) = \rho_m - 1.68 \times 10^{-4} (T - T_m) - 1.74 \times 10^{-7} (T - T_m)^2$$

with T_m and ρ_m being 1687 K and 2.53 gr/cm^3 respectively. The hemispherical total emissivity of molten silicon at the melting temperature was determined to be 0.18 , and the constant pressure specific heat capacity was evaluated as a function of temperature. The surface tension of molten silicon over a similar temperature range is expressed by

$$\sigma(T) = 875 - 0.22 (T - T_m) \text{ mN/m.}$$

NOMENCLATURE

c_p	constant pressure specific heat capacity
m	sample mass
n	integer
r	radial coordinate of sample surface
r_0	radius of sphere
ϵ_n	amplitude of n -th mode oscillation
t	time
A	surface area of the sample
Q	net sample charge
T	temperature in K
T_e	environmental temperature in K
T_m	melting temperature in K
V	volume of sample
ϵ_T	hemispherical total emissivity
ρ	density
ρ_m	density at melting temperature
σ	surface tension
σ_{SB}	Stefan-Boltzmann constant

INTRODUCTION

Accurate thermophysical property values of molten silicon are important ingredients in numerical modeling of crystal growth process. As dimensions of semiconductor devices continue to shrink, needs for high quality crystals are ever increasing, and understanding and controlling the formation kinetics of various crystal defects such as point defects and impurity distribution in a grown crystal became very important.

In this paper, density, specific heat, and surface tension of molten silicon which were measured using the HTESL will be presented. By isolating the sample from container walls the silicon melt undercooked as much as 300 K . In addition, the hemispherical total emissivity at melting temperature has been evaluated using a known literature value of specific heat capacity of molten silicon at the melting temperature.

The main apparatus which was used for the present experiments was the HTESL [1] at JPL. The capability of levitating non-conducting as well as conducting materials is very unique to this levitator. Since the system operates in a high vacuum, sample purity is maintained, and melts undercool deeply. Some of the characteristics of the HTESL, which made the present work possible are: (i) it could levitate pure silicon samples, melted them while in levitation, and could reach undercooked states, (ii) sample heating and levitation do not interfere, each other so that sample could be cooled in a purely radiative manner when heating source was either turned off or blocked. This allowed description of the whole cooling process by a well defined heat transfer equation. (iii) Levitated drop is quiescent and maintains an axis-symmetric shape along vertical direction. In reality, samples show slightly prolate spherical shape due to surface charges. Extent of asphericity depends on the apparent surface tension, radius, and mass density of the drop. In the case of a molten silicon 2 mm in diameter, the asphericity was less than 1% .

EXPERIMENTAL PROCEDURES

The HTESL levitates a sample 1 to 3 mm in diameter between parallel plate electrodes spaced about 10 mm apart. The electrode assembly is housed by a stainless steel chamber which is typically evacuated to 10^{-8} Torr before sample heating began. Samples are heated using a 1-kW xenon arc lamp. Detailed description of the HTESL is given in an earlier publication [1].

Once a levitated sample is melted, the molten sample shows very nearly spherical shape due to the action of surface tension. In order to maintain clean surfaces during processing, it was necessary to begin with pure, clean samples. Silicon samples were prepared from 99.9995%

1) Presently at the Space Systems, Loral, Palo Alto, CA

2) Department of Engineering, Harvey Mudd College

pure stock from Johnson-Matthey. These were then ground roughly into spheres. They were cleaned by immersion in 5% HF at room temperature for 5 minutes, rinsed in distilled water, and finally rinsed in anhydrous ethanol. The samples' masses were approximately 10 mg.

Since the levitation mechanism of HTESL does not affect the sample temperature, a sample that is heated by a radiant heating source will cool purely radiatively when the heating source is blocked, and the ensuing cooling process can be described by the well defined radiative heat transfer equation

$$mc_p \frac{dT}{dt} = -\sigma_{sb} \epsilon_T A (T^4 - T_E^4). \quad (1)$$

The fact that accurate measurement of c_p/T is possible from Eq. (1) is one of important merits of the HTESL.

When a levitated sample is fully molten, different experiments are conducted at various thermal conditions. Experiments for mass density and specific heat capacity of molten silicon were initiated by blocking the heating source and allowed the silicon melt freely cool into undercooked states until the **recalcescence** took place. Upon beam blocking, both temperature measurement (by a pyrometer) and image recording by a video system went on simultaneously throughout cooling process. A typical temperature versus time profile for a silicon melt obtained during such a cooling process is shown in Fig. 1. The melt started cooling from about 100 K above the melting temperature and undercooked as much as 300 K before **recalcescence** took place. Upon **recalcescence** the sample temperature **ris**ed sharply and reached isotherm state. Unlike many pure metals, Fig. 1 does not show constant radiance over the isotherm region. This is attributed to changing spectral **emissivity** in this region. Discontinuities in temperature gradient due to phase transition is clearly identifiable in a magnified view as shown in Fig. 2. Output of the single color pyrometer operating at 700 nm was calibrated using **Wien's law** taking the temperature immediately following the **recalcescence** as its melting temperature ($T_m = 1687$ K). Also, constant spectral

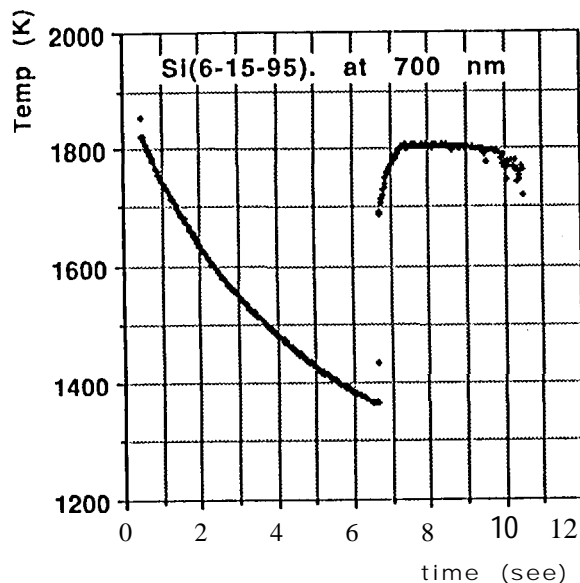


Fig. 1 A typical temperature versus time profile for a silicon melt undergoing purely radiative cooling process.

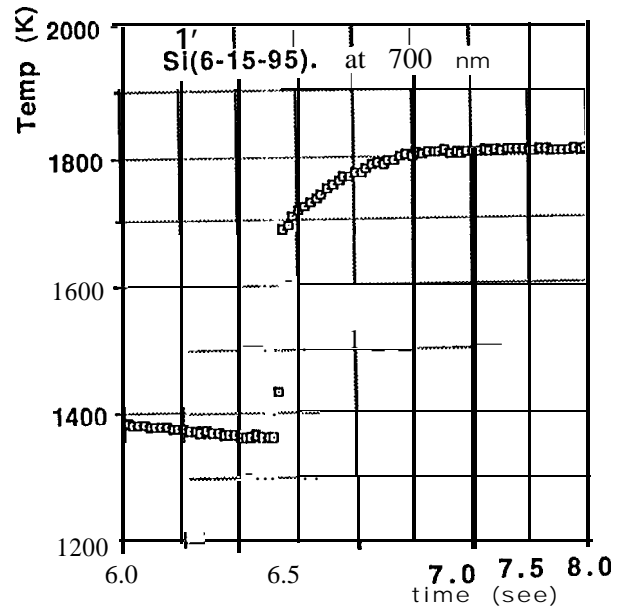


Fig. 2 A magnified view of Fig. 1 around the recalcescence event.

emissivity of the melt over the liquid temperature range was assumed.

The sample temperature so obtained during cooling process was correlated to the video images so that each sample size could be related to its corresponding temperature.

For surface tension measurement, small sinusoidal electric field was superimposed to levitation field and resonant oscillation was searched by sweeping the ac field frequency. When a resonance is found, the mode of oscillation was identified and the frequency at the maximum oscillation amplitude was recorded along with sample temperature.

Surface charge on a levitated drop modifies the apparent surface tension, and the drop oscillation frequency should reflect this. If we know the net drop charge and measure the lowest resonant oscillation frequency, one can use the Rayleigh's expression for charged drop oscillation [2],

$$\omega = \left[\frac{8\sigma}{\rho r_o^3} \left(1 - \frac{Q^2}{16\pi r_o^3 \sigma} \right) \right]^{\frac{1}{2}}, \quad (2)$$

and the true surface tension σ may be extracted from this equation. Effects on surface tension due to non-uniform charge distribution and deviation from a perfect spherical shape were corrected using the perturbational analysis of electrostatically levitated drops by J. Feng et. al. [3].

MASS DENSITY MEASUREMENT

The basic approach for the density measurements was consisted of (i) digitization of recorded video images, (ii) edge detection, and (iii) calculation of the area (therefore, the volume of the sample) through linear spherical harmonic fit. The density is then obtained using the sample mass which was measured immediately following the experiment. Detailed description of the image analysis method used in this experiment will be published elsewhere[4].

Figure 3 shows the result of our density measurements of molten silicon over 400 K span. Unlike pure metals it shows quadratic nature which can be fit using the following equation:

$$\rho(T) = \rho_m - 1.68 \times 10^{-4} (T - T_m) - 1.74 \times 10^{-7} (T - T_m)^2 \quad (2)$$

with the melting temperature, $T_m = 1687$ K, and the density at the melting temperature $\rho_m = 2.53 \text{ gr/cm}^3$. It is surprising to see from Eq. (2) that, while the density at the melting temperature agrees well with reference value of

2.53, $(\frac{\partial \rho}{\partial T})_T$ at T_m is two times smaller in magnitude than

the reference value of -3.5×10^{-4} which is given in the Lids and Guthrie's book [5]. The reference did not provide the range of variation among various data. We are in a process of carefully combing through the imaging and analysis processes we used in search of any systematic error which might account for such a difference.

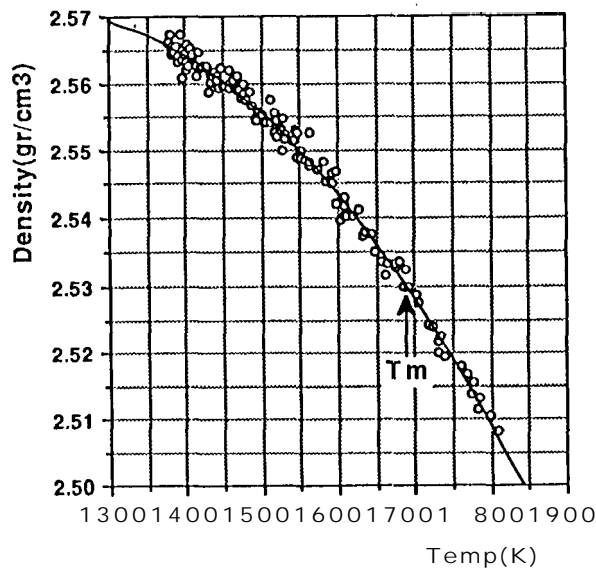


Fig. 3 Density of molten silicon as a function of temperature.

SPECIFIC HEAT MEASUREMENT

Constant pressure specific heat capacity is a very important thermodynamic parameter from which all other parameters such as enthalpy, entropy, and Gibbs free energy can be derived. These quantities measured in undercooked regions of various materials carry special implications for the studies of solidification processes and for the selection of metastable phases. In spite of their importance, specific heat capacity and hemispherical total emissivity are known for very few high-temperature liquids. Data is particularly scarce for undercooked liquids since they immediately solidify when placed in contact with most crucibles. The HTESL allows accurate determination of c_p/ϵ_T in a simple heat transfer environment while the levitated melt cools to undercooked states. Rearrangement of Eq. (1) gives

$$\frac{c_p}{\epsilon_T} = - \frac{\sigma_{SB} A (T^4 - T_E^4)}{m \frac{dT}{dt}} \quad (3)$$

Using Temperature-time profile obtained experimentally (such as shown in Fig. 1), and also evaluating dT/dt from it, c_p/ϵ_T can be readily obtained, and it is shown in Fig. 4.

From this, $c_p(T)$ can be determined if $\epsilon_T(T)$ is known, and conversely, $\epsilon_T(T)$ can be found if $c_p(T)$ is known [6].

Frequently specific heats are known at their melting temperature while hemispherical total emissivities are not. In such cases, $\epsilon_T(T_m)$ at the melting temperature can be obtained. The literature value of the constant pressure specific heat capacity of molten silicon at the melting temperature is 25.61 Joule/mole/K. From Fig. 4 with the use of $c_p(T_m) = 25.61$ Joule/mole/K, we obtained $\epsilon_T(T_m) = 0.18$ for the hemispherical total emissivity at the melting temperature. There are very few published data to which the present value can be compared. However, our earlier result [6] showed $\epsilon_T(T_m) = 0.1710.01$ which is in good agreement with the present result,

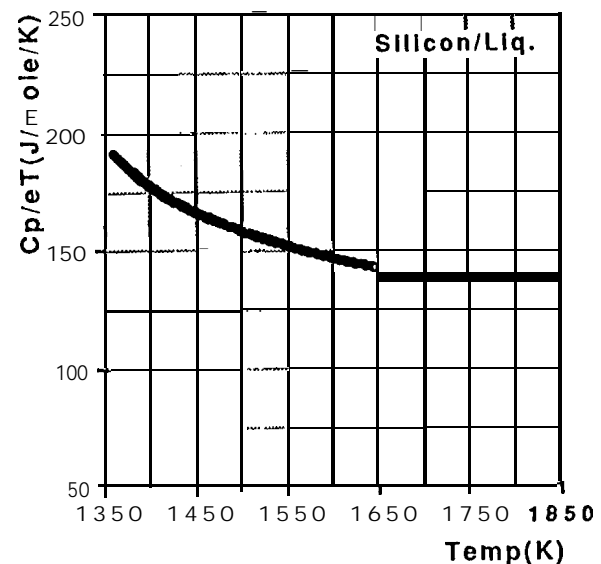


Fig. 4 C_p/ϵ_T VS. temperature of molten silicon as calculated from Fig. 1.

Strictly speaking $\epsilon_T(T)$ has to be independently measured as a function of temperature to evaluate $c_p(T)$.

Since $\epsilon_T(T)$ is not available at the present time, let us assume that it remains constant at $\epsilon_T(T_m) = 0.18$ throughout liquid region, and calculate $c_p(T)$ over the same temperature region. In fact, such assumption is not totally unreasonable if one considers that spectral emissivities of molten silicon measured by Krishnan et. al. [7] using ellipsoidal polarimeter technique showed almost no temperature dependency. Fig. 5 shows $c_p(T)$ as a function of temperature so obtained. Non linearly decreasing trend of $c_p(T)$ with rising temperature seems to be a characteristic of molten silicon which contrasts to rather linear behavior shown by many pure metals. [6]

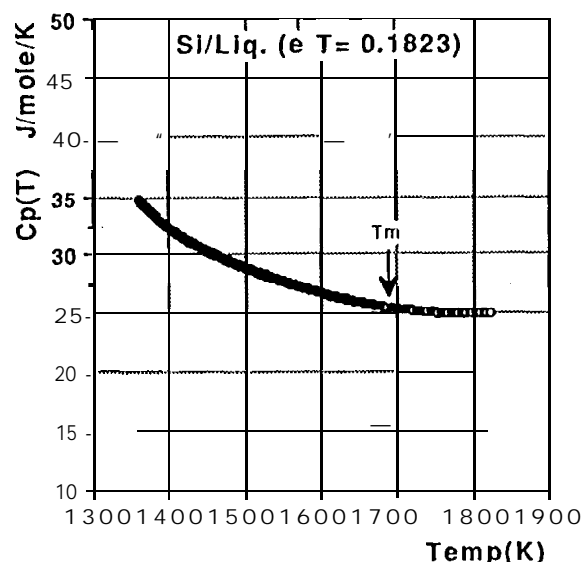


Fig. 5 $c_p(T)$ vs. temperature calculated from Fig. 4 assuming $\epsilon = 0.18$.

SURFACE TENSION

Spherical shape of melts levitated by the HTESL greatly simplifies the analysis of surface tension measurements. In view of the fact that surface tension is particularly sensitive to even minute surface contamination, HTESL operating in a high vacuum environment would be ideal for measuring surface tension, particularly of those chemically reactive materials.

Unlike experiments previously described, in this experiment we had to fix the sample temperature at a predetermined value using a different pyrometer (manufactured by E²T and operating at 4 μm wavelength) so that we could measure temperature even in the presence of intense radiation from the xenon lamp.

Fig. 6 shows our experimental result on surface tension of molten silicon as a function of temperature. The data could be fit by an equation

$$\sigma(T) = 875 - 0.22 (T - T_m) \text{ mN/m.} \quad (4)$$

The present result shows the surface tension at the melting temperature to be 875 mN/m which is comparable with 885 mN/m obtained by Hardy [8] using sessile drop method, but it is much greater than 783.5 mN/m obtained by Pryzborowski et. al. [9] using electromagnetic levitation method. As for $-d\sigma(T)/dT$, the present result shows 0.22 mN/m/K while references [8] and [9] show 0.28 and 0.65, respectively. At the present time, it is too premature to prefer a particular result. Only a more comprehensive experiment which is designed to embrace all specific experimental conditions involved in all different experimental approaches would be able to provide causes of these different results.

DISCUSSION

We have presented our data on density, hemispherical total emissivity, constant pressure specific heat capacity, and surface tension of molten silicon over 400 K range around the melting temperature. These experiments were carried out for the first time using the HTESL which was recently developed at JPL. By no

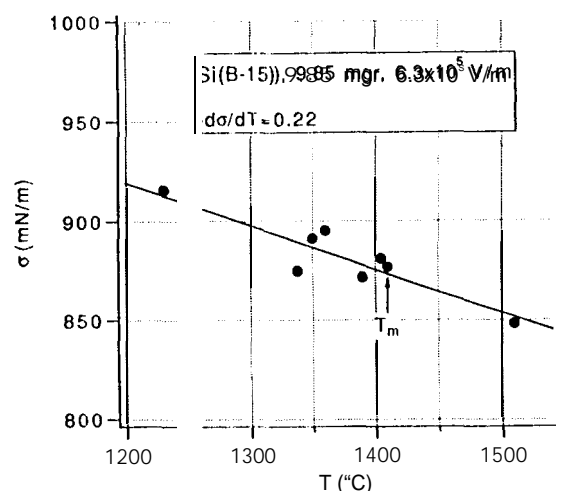


Fig. 6. Surface tension $\sigma(T)$ of molten silicon as a function of temperature.

means we are satisfied with these results. In particular, the density data is quite puzzling. Also, another round of surface tension measurement experiment is being planned at this time. This and other puzzling issues will be addressed in a later publication. One thing certain, however, is that we found a new tool called "HTESL" for measurements of thermophysical properties of molten silicon which showed a potential of producing high quality data.

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REFERENCES

- [1] W. K. Rhim, S. K. Chung, D. Barber, K. F. Man, G. Gutt, A. Rulison, and R. E. Spjut, *Rev. Sci. Instrum.*, 64, 2961, 1993
- [2] J. W. S. Rayleigh, *Phil. Mag.*, 14, 184-186, 1882.
- [3] J. Q. Feng and K. V. Beard, *Proc. R. Soc. London A.*, 430, 133, 1990
- [4] S. K. Chung, D. Thiessen, Y. J. Kim and W. K. Rhim, "A non-contact measurement technique for the density and the thermal expansion of undercooled and superheated materials," *Rev. Sci. Instrum.* (to be submitted)
- [5] T. Lids and R. I. Guthrie, *The Physical Properties of Liquid Metals*, Oxford University Press, 1988
- [6] A. J. Rulison and W. K. Rhim, *Metal. and Materials Trans.* (in press)
- [7] S. Krishnan, J. K. R. Weber, P. C. Nordine, R. A. Schiffman, R. H. Hauge and J. L. Margrave: *High Temp. Science*, 30, 137, 1991
- [8] S. C. Hardy, *J. Crystal Growth*, 69, 456, 1984.
- [9] M. Pryzborowski, T. Hibiya, M. Eguchi, and I. Egry, *J. Japan. Assoc. Crystal Growth*, 21(3), 224, 1994.